

Title	DV-X Calculation on Energy Levels for SF
Author(s)	Nakamatsu, Hirohide; Adachi, Hirohiko; Mukoyama, Takeshi
Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1991), 68(5-6): 304-308
Issue Date	1991-02-28
URL	http://hdl.handle.net/2433/77356
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

DV-X α Calculation on Energy Levels for SF₆

Hirohide NAKAMATSU*, Hirohiko ADACHI** and Takeshi MUKOYAMA***

Received November 8, 1990

Energies of valence and inner-shell levels for SF₆ are derived with the discrete variational X α method. The energies in the ground state and the transition state are calculated by the methods of self-consistent-charge. In the transition state, spin-polarized effects are also examined. The effects are negligible for the valence levels and large for the inner-shell levels. The theoretical orbital ionization energies in the transition state agree with the experimental energies in photoelectron spectra within 1 eV for F 2*p* levels and within 8% for the other levels.

KEY WORDS: SF₆/ Molecular orbital calculation/ Discrete variational X α method/ Photoelectron spectra/

I. INTRODUCTION

Since SF₆ molecule is a chemically stable and structurally simple molecule, its electronic structure has been studied extensively. The X-ray photoelectron spectra (XPS) for its valence levels have been measured at high resolution.¹⁾ It also attracts renewed attentions to its outstanding shape resonances, which are observed in the spectra of excitation to unoccupied levels such as X-ray absorption spectra and electron energy loss spectra.²⁾ The shape resonance is one of basic phenomena for understanding the X-ray absorption near-edge structure (XANES).³⁾

We have been reported the energies of shape resonances in the X-ray absorption spectra⁴⁾ and cross section of XPS for SF₆,⁵⁾ using the DV-X α method. The results show a distinct assignment to the occupied and unoccupied molecular orbitals. The absolute energies of ionization, however, have not been discussed yet in a series of our works. In the present work, ionization energy of each molecular orbital will be derived from DV-X α method and compared with the value obtained with the X-ray photoelectron spectroscopy.

II. COMPUTATIONAL METHOD

The computational details of the DV-X α method used in the present work have been described elsewhere.⁶⁾ The points of the method for the present calculation are as follows. In the DV-X α method, matrix elements in the secular equation are derived from weighted sum of integrand values at sampling points. Numerical atomic orbitals derived from isolated atoms were used as basis sets. They

* 中松 博英: Laboratory of Nuclear Radiation, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611.

** 足立 裕彦: Hyogo University of Teacher Education, Shimokume, Yashiro-cho, Kato-gun, Hyogo 637-14.

*** 向山 毅: Laboratory of Nuclear Radiation, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611.

are reasonably good basis functions in the molecular potentials. A large number of atomic orbitals as an extended basis set are preferable to get better eigenfunctions and eigenvalues. To obtain atomic orbitals with high quantum numbers easily, a spherical potential was superimposed upon the atomic potential as follows:

$$\begin{aligned} V^i(r) &= V_a^i(r) - V_s^i & \text{for } r \leq R_s^i, \\ &= -c/r & \text{for } r > R_s^i, \end{aligned} \quad (1)$$

where $V_a^i(r)$ was the potential of i th atom, V_s^i the potential depth and R_s^i the radius. Coulomb potential $-c/r$ was assumed outside of the sphere. The c was adjusted to link the two potentials at $r=R_s^i$.

The basis set for SF₆ consisted of 1s to 4p for the sulfur atom and 1s to 3p for the fluorine atoms. The Slater exchange parameter was chosen to be $\alpha=0.7$ for all the present calculations. The SF₆ molecule was considered in the O_h symmetry with the S-F bond length of 156.4 pm.⁷⁾

The self-consistent charge (SCC)⁸⁾ method was used to approximate the complete self-consistent field. Overlap charges are partitioned into atomic charge densities by the use of the Mulliken population analysis in the SCC method. The atomic electron densities are employed to give molecular potential for the next iteration. The numerical basis functions were generated in the each iteration. The atomic potentials for the basis functions were derived from the atomic charge densities through the Mulliken population analysis (SCC-I), as well as those for the molecular potential. In another way, taking account of the potential tail of the neighboring atoms, the atomic potentials were obtained from the spherical average of the molecular charge density around the nuclei (SCC-II).

The relaxation on the ionization was obtained from the difference between the orbital ionization energy and the orbital energy in the ground state. In the X α method, it is usual to calculate the ionization energy on the basis of the transition state method,⁹⁾ i.e. half electron is removed from the orbital concerned. On the ionization, spin is polarized in the molecule in contrast to that in the ground state where SF₆ molecule has a closed shell electronic structure. The computational procedure for the spin-polarized case is very similar to that for the non-spin-polarized.¹⁰⁾ The relaxation and the spin-polarization on the ionization were evaluated separately.

III. RESULTS AND DISCUSSION

The orbital energies in the ground state and the transition state are shown in Table 1 and an illustrative comparison is shown in Fig. 1. In the SCC-I method, the non-spin-polarized calculations with the transition state give the relaxation energies about 3.9 eV for the valence levels. The value agrees with that derived from the multiple scattering X α method by Connolly and Johnson.¹³⁾ The relaxation energies of the valence levels are equal to those derived from the spin-polarized calculation, while on the other hand the spin-polarization increases the energies of the inner-shell levels on the transition. The numbers of up- and down-spin electrons were almost equal in the transition state of valence levels, which phenomenon is

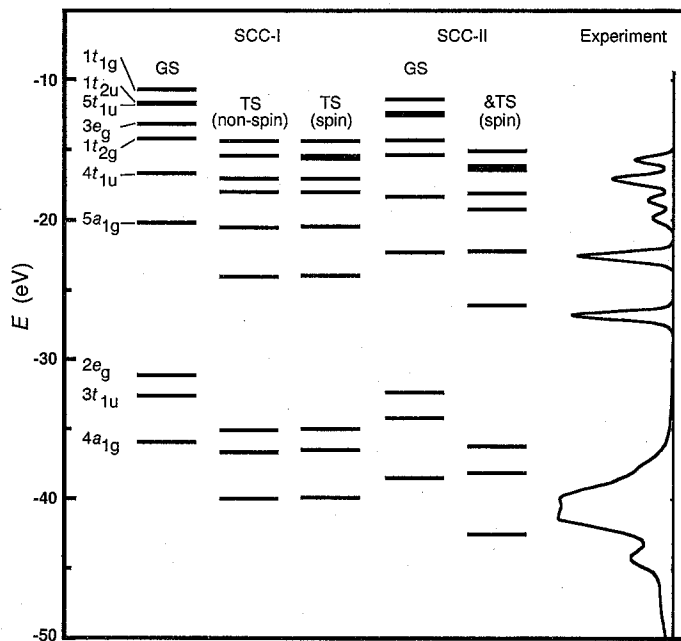


Fig. 1. Comparison of level energies. The abbreviations are the same as those in Table 1. The experimental spectrum is a duplicate of that in Ref. 1.

Table 1. Orbital energies in ground state and transition state

MO	AO**	SCC-I				SCC-II			Exper.***
		GS	TS	TS (spin)	(ΔE)	GS	&TS (Spin)	(ΔE)	
$6a_{1g}$	S $3s$	-2.6				-5.2			
$1t_{1g}$	F $2p$	-10.7	-14.4	-14.4	(1.3)	-11.4	-15.1	(0.6)	-15.7
$1t_{2u}$	F $2p$	-11.7	-15.5	-15.5	(1.5)	-12.4	-16.2	(0.8)	-17.0
$5t_{1u}$	F $2p$	-11.8	-15.5	-15.6	(1.4)	-12.6	-16.4	(0.6)	-17.0
$3e_g$	F $2p$	-13.2	-17.0	-17.0	(1.6)	-14.3	-18.1	(0.5)	-18.6
$1t_{2g}$	F $2p$	-14.2	-18.0	-18.0	(1.8)	-15.4	-19.2	(0.6)	-19.8
$4t_{1u}$	F $2p$	-16.7	-20.6	-20.5	(2.2)	-18.4	-22.2	(0.5)	-22.7
$5a_{1g}$	F $2p$	-20.2	-24.1	-24.0	(3.0)	-22.3	-26.1	(0.9)	-27.0
$2e_g$	F $2s$	-31.1	-35.1	-35.0	(4.3)	-32.3	-36.2	(3.1)	-39.3
$3t_{1u}$	F $2s$	-32.6	-36.6	-36.5	(4.7)	-34.2	-38.1	(3.1)	-41.2
$4a_{1g}$	F $2s$	-35.9	-40.0	-39.9	(4.3)	-38.5	-42.5	(1.7)	-44.2
$2t_{1u}$	S $2p$	-164.3	-180.4	-179.2	(1.6)	-172.6	-187.5	(-6.7)	-180.8*
$3a_{1g}$	S $2s$	-211.2	-231.7	-230.6	(14.1)	-225.4	-244.8	(-0.1)	-244.7
$1e_g, 1t_{1u}$, $2a_{1g}$	F $1s$	-660.1	-700.0	-690.7	(3.9)	-659.9	-690.5	(4.1)	-694.6
$1a_{1g}$	S $1s$	-2401.6	-2488.6	-2473.1	(17.0)	-2410.7	-2482.2	(7.9)	-2490.1

GS: ground state, TS: transition state

ΔE : difference from experimental energy

* Weighted average of $2p_{1/2}$ and $2p_{3/2}$

** Main AO components

*** Ref. 1, 11, 12

interpreted as wide distribution of the valence electrons. Thus the spin-polarization effect is negligible for the valence levels.

In the SCC-II method, the orbital energies for the inner shell in the ground state are lower than those in the SCC-I method. Atomic orbitals with large radii contribute the potentials of adjacent atoms. This contribution may increase the orbital energies in the SCC-I method. The relaxation energies on the ionization which are derived from the spin-polarized calculation with the SCC-I method are added on the SCC-II results of the ground state. These results are denoted as SCC-II &TS (spin) in Table 1 and Fig. 1. Compared with the SCC-I method, the SCC-II method results in better agreement where the levels shift to the lower energy side. The energy differences from the results of the photoionization experiments are shown as ΔE . For the F2*p* valence levels, the differences are less than 1eV, that is 5% of ionization energy. For the F2*s* levels and the other levels, they are less than 8%.

A large discrepancy appears in the interval of sulfur 2*s* and 2*p*. The estimated interval is 57.3eV as opposed to the experimental value of 63.9eV. An experiment of the sulfur gas gives the equivalent interval of 65eV.¹⁴⁾ Similar disagreement is seen in the results of atomic calculations by Hartree-Fock-Slater method,¹⁵⁾ which gives 52.8eV. The interval of argon 2*s* and 2*p* has a similar discrepancy in the

Table 2. Orbital energy variation with radius of potential added in atomic orbital calculation. Energy differences (eV) of each level from the corresponding level with $r(\text{well})=7a_u$ are shown.

$r(\text{well})^*$	7.0	3.5	5.0	8.0	9.5	11.0	14.0	20.0
Diff.**		1.1	3.7	-0.3	-0.2	0.8	1.4	1.9
MO								
6 <i>a</i> _{1g}	-5.2	0.5	0.9	0.3	2.5	0.5	0.5	0.3
1 <i>t</i> _{1g}	-11.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1 <i>t</i> _{2u}	-12.4	0.0	0.0	0.0	2.0	0.0	0.0	0.0
5 <i>t</i> _{1u}	-12.6	0.0	0.0	0.0	2.1	0.0	0.0	0.0
3 <i>e</i> _g	-14.3	0.2	0.4	0.1	0.5	0.4	0.5	0.2
1 <i>t</i> _{2g}	-15.4	0.1	0.4	0.1	0.2	0.2	0.3	0.2
4 <i>t</i> _{1u}	-18.4	0.2	0.8	0.2	0.2	0.3	0.3	0.2
5 <i>a</i> _{1g}	-22.3	0.4	0.9	0.3	0.3	0.4	0.4	0.3
2 <i>e</i> _g	-32.3	0.3	0.6	0.1	0.3	0.3	0.3	0.2
3 <i>t</i> _{1u}	-34.2	0.3	0.8	0.2	0.2	0.3	0.3	0.3
4 <i>a</i> _{1g}	-38.5	0.7	1.6	0.4	0.3	0.6	0.7	0.5
2 <i>t</i> _{1u}	-172.6	2.5	5.9	1.6	0.0	2.2	2.0	1.8
3 <i>a</i> _{1g}	-225.4	2.5	5.8	1.6	0.0	2.1	1.9	1.8
1 <i>e</i> _g , 1 <i>t</i> _{1u} , 2 <i>a</i> _{1g}	-659.9	-0.2	0.1	0.0	0.0	0.0	0.1	-0.2
1 <i>a</i> _{1g}	-2410.7	2.7	6.9	1.9	0.4	2.7	2.5	2.2

* Radii of added potentials in atomic units

** Energy differences of 1*t*_{1g} from that with $r=7a_u$

*** Main AO components

results by the transition state method¹⁶⁾ but agrees with the experimental when the ionization energies are derived using 4SCF procedure.¹⁷⁾ The discrepancy of the inner-shell energies may come from the approximation in the transition state method.

We examine the energy dependence on the radius of the spherical potential added on the atomic potentials as described in Eq. 1. The spherical potential affects the atomic orbitals. It may not affect the results of the molecular orbital calculations when the basis set is large enough. For the present basis set, the energy dependence occurs as shown in Table 2. In the present examination, the radius of 7.0 au is preferable. First, ionization energies of $1t_{1g}$ orbitals, that is the first ionization energies, are compared with the value calculated with the radius of 7.0 au. The radii from 7.0 to 9.5 au give a minimum energy. Next, the differences of each level from the corresponding level with $r=7.0$ au are shown in Table 2, after the energies of levels are shifted for normalization in such a way that the first ionization energies agree with each other. For the valence levels from $1t_{1g}$ to $4a_{1g}$, the energy differences are almost equal to zero except for some levels with the radius of 5.0 and 9.5 au. For the inner shell, the levels are a few eV higher than those with the radius of 7.0 au. In all the radii, the radius of 7.0 au gives lower energies and is preferable for atomic orbitals to represent the molecular orbitals in the present calculations. The values calculated with the radius of 7.0 au are employed for the calculation of the SCC-II method in Table 1 and Fig. 1.

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